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(54) MANUFACTURE OF PLASTICS DISPERSIONS

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(57) CLAIM 1. A process for the preparation of aqueous plastics dispersions suitable for making paints having a high wet adhesion, by copolymerization in an aqueous medium under conventional conditions of the following monomers:

A) from 20 to 79,4% by weight, preferably 40 to 60% by weight, calculated on the total quantity of the monomers, of the hardening monomers methyl methacrylate, styrene and vinyl toluene or a mixture thereof,

B) 20-99,4% by weight, preferably 40 to 60% by weight, calculated on the total quantity of the monomers, of monomers, having a plasticizing effect in the polymer, selected from the group of acrylic acid esters carrying in the alcohol radical a linear or branched alkyl radical having from 2 to 8 carbon atoms or conjugated dienes having from 4 to 8 carbon atoms optionally substituted by halogen,

from 0,1 to 5% by weight of acrylic acid, methacrylic acid, acrylamide, methacrylamide or mixtures of these, which

*composition
of example
2 stand.*

✓ Syrene

20-99,4

✓ Acrylate
20-99,4

✓ acid
0,1-5

This invention relates to a process for the manufacture of plastics dispersions suitable for making dispersion paints having a good wet adhesion, i.e. when wetted after drying.

The problem of the wet adhesion, i.e. the adhesion of dried paints on wetting, of dispersion paints on smooth non-absorbent surfaces has limited for a long time the use of such dispersion paints. Dispersion paints having a low pigment content, which dry on the substrate with formation of a glossy or slightly dull film, have a poor adhesion to smooth non-absorbent surfaces when the paints are rewetted after drying. The wet adhesion is especially unsatisfactory with fresh paints which have not yet undergone ageing.

Dispersion paints of low pigment content are chosen when a washable coat of paint is desired. Owing to the high binder content of the paint a closed washable film is formed. Dispersion paints drying with formation of a glossy or slightly dull film also have a concentration by volume of pigment of less than 40 %, generally the concentration is in the range of from about 10 to 25 %. They also contain about 3 to 15 % of organic solvents to improve the gloss and flow, to prolong the working time and for film consolidation, for example polyhydric alcohols miscible with water and having up to 6 carbon atoms, especially ethylene and propylene glycol, or the monomethyl to monobutyl ethers thereof. To improve the film consolidation solvents having a restricted solubility in water are used, such as the monoglycol esters of carboxylic acids and more particularly esters of carboxylic acids with monoalkyl ethers of glycols or oligoglycols. Butyl diglycol acetate is one of the most widely used representatives of this group. The combination of a low

pigment content with a relatively high solvent content has a very detrimental effect on the wet adhesion of the coats of dispersions paints.

With a poor wet adhesion paints formulated to give washable coats do not have this property when applied to smooth non absorbent surfaces, for example old coats of alkyd or oil paint. In moist rooms, such as kitchen, bath rooms, or industrial places, where water of condensation may form, the new coat may detach from the substrate if the wet adhesion is not sufficient. Moreover, a poor wet adhesion complicates painting. When, for example, the base and the upper half of a wall or the wall and the ceiling are to be painted in different colors, the first coat of paint may be soiled with the different paint by slipping of the brush. In principle, the different paint could be wiped off with a wet cloth, but with a poor wet adhesion the first paint may then be damaged or even removed simultaneously.

Therefore, many attempts have been made to modify plastics dispersion in such a manner that the dispersion paints made therewith have the desired wet adhesion. In German Offenlegungsschrift 1,595,501 it has been proposed to prepare plastics dispersions by polymerizing suitable monomers in aqueous emulsion using as comonomers 0.2 to 15 % by weight, calculated on the total amount of the monomers, of compounds carrying oxirane groups and then to react the copolymer at room temperature with ammonia or an amine. Suitable oxirane compounds are above all, glycidyl esters of acrylic or methacrylic acid and allyl glycidyl ethers or vinyl glycidyl ethers.

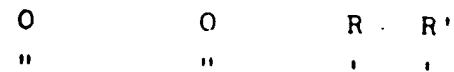
Dispersion paints prepared with plastics dispersions of this type have quite a good wet adhesion, but for many applications

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the wet adhesion is not all sufficient.

The present invention provides a process for the preparation of aqueous plastics dispersions suitable for making paints having a high wet adhesion, by copolymerization in an aqueous medium under conventional conditions of the following monomers:

- A) from 20 to 79.4% by weight, preferably 40 to 60% by weight, calculated on the total quality of the monomers, of the hardening monomers methyl methacrylate, **styrene** and vinyl toluene or a mixture thereof,
- B) from 20 to 79.4% by weight, preferably 40 to 60% by weight, calculated on the total quantity of the monomers, of monomers having a plasticizing effect in the polymer, selected from the group of **acrylic acid esters** carrying in the alcohol radical a linear or branched alkyl radical having from 2 to 8 carbon atoms or conjugated dienes having from 4 to 8 carbon atoms optionally substituted by halogen,
- C) from 0.1 to 5% by weight of **acrylic acid**, **methacrylic acid**, acrylamide, methacrylamide or mixture of these, which comprises using additionally in the polymerization
- D) from 0.5 to 10% by weight of an acetoacetic acid ester of the formula



wherein R is H or CH_3 , R' is H or CH_3 , and X is $-\text{O}-$, $-\text{O}-\text{CH}_2$ or $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}-$.

Hardening monomers of the kind cited subA) are for

ex-

ample methylmethacrylate, styrene or vinyltoluene.

Plasticizing monomers of the kind sub A) are for example ethyl acrylate, isopropyl acrylate, butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate or butadiene, isoprene or chloroprene.

Among water-soluble monomers of the kind cited sub C) there may be mentioned, by way of example acrylic acid, methacrylic acid, acrylamide or methacrylamide.

Suitable monomers of the kind cited sub D) are, for example acetoacetic acid vinyl ester, acetoacetic acid allyl ester or acetoacetic acid esters of β -hydroxyethyl acrylate or methacrylate or hydroxypropylacrylate or methacrylate. Acetoacetic acid allyl ester is used preferably, as it yields the best results.

For dispersions prepared in an acid range it is often advantageous for improving their storage life and for facilitating the preparation of paints to adjust the pH to a value in the range of from 7.5 to 10 with ammonia or suitable amines for example water-soluble tertiary amines.

Plastics dispersions are extremely complex systems. The preparation of the dispersions according to the invention of high-quality requires the application of the experiences made hitherto in the field of the emulsion polymerization, including those which are not described herein in detail. A disregard of the principles known to an expert in the field of emulsion polymerization may therefore detrimentally affect important properties such as the resistance to water, of the dispersion films or the films of the coats of paint. For this reason the conventional content of ionic emulsifiers of up to 3 %, preferably of up to 2 % in the dispersions or of non-ionic emulsifiers of up to 6 %,

preferably of up to 4 % should not be exceeded substantially.

Suitable non-ionic emulsifiers are, for example, alkyl polyglycol ether such as the ethoxylation products of lauryl, oleyl or stearyl alcohol or of mixtures such as coconut fatty alcohol; alkyl phenol polyglycol ethers such as the ethoxylation products of octyl- or nonyl-phenol, diisopropyl-phenol, triisopropyl-phenol or di- or tri-tert.butyl-phenol; or ethoxylation products of polypropylene oxide.

As ionic emulsifiers anionic emulsifiers are used in the first place, for example alkali metal or ammonium salts of alkyl, aryl or alkylaryl sulfonates, sulfates, phosphates, phosphonates, or compounds having different anionic end groups. oligo- or polyethylene oxide units possibly being contained between the hydrocarbon radical and the anionic group. Typical representatives are sodium lauryl sulfate, sodium octyl-phenol glycol ether sulfate, sodium dodecyl-benzene sulfonate, sodium lauryl diglycol sulfate, ammonium tri-tert.butyl-phenol penta- or octa-glycol sulfate.

As protective colloids there may be used natural substances such as gum arabic, starch, alginates or modified natural substances such as methyl, ethyl, hydroxyalkyl, or carboxymethyl cellulose, or synthetic substances, for example polyvinyl alcohol, polyvinyl pyrrolidone, or mixtures of the aforesaid substances. Modified cellulose derivatives and synthetic colloids are preferred.

These protective colloids can only be employed to a limited degree if the described monomer systems are used, as it is known to one skilled in the art. The quantities used are frequently low, namely in the range from 0.001 to 1 % and the tolerance and

the kind of addition must be examined in each case. When the use of protective colloids is required, the principles, for example disclosed in German Auslegeschrift No. 1,570,312 may be applied.

5 To initiate and continue polymerization oil-soluble and/or
 16.64276 preferably water-soluble radical forming agents or redox systems
 10 are used, for example hydrogen peroxide, potassium or ammonium peroxydisulfate, dibenzoyl peroxide, lauryl peroxide, tri-tert.
 15 butyl peroxide, bisazodiisobutyronitrile, either singly or together with reducing components, for example sodium bisulfite,
 20 (Registered trade mark)
 Rongalite , glucose, ascorbic acid, and other compounds having a reducing action.

25 The special advantage of the dispersions prepared according to the invention resides in the fact that they are not only suitable for the manufacture of gloss dispersion paints having a good wet adhesion on non-absorbent surfaces, but that they have moreover a high resistance to saponification.

30 The following examples illustrate the invention:

E X A M P L E 1:

35 Firstly a monomer emulsion was prepared having the following composition:

310 parts by weight water

40 6 parts by weight sodium salt of lauryl alcohol diglycol ether sulfite

45 12 parts by weight methacrylic acid

50 6 parts by weight acrylic acid

55 300 parts by weight butyl acrylate

60 300 parts by weight styrene and

65 12 parts by weight acetoacetic acid allyl ester.



The components were stirred in a rapid stirrer until a stable emulsion was obtained.

A mixture consisting of
303 parts by weight water

5 3 parts by weight sodium salt of lauryl alcohol diglycol ether sulfate and

16.64276 60 parts by weight of the monomer emulsion
was heated in a 2 liter three-necked flask placed in a heating
bath and equipped with a stirrer, a reflux condenser, a dropping
funnel and a thermometer and a solution of 0.45 parts by weight
ammonium peroxydisulfate in 15 parts by weight water was added.
Thereafter the residual monomer emulsion was added and polymeri-
zation was carried to completion. The total time of addition
was 2 hours, the polymerization temperature and the temperature
during the second heating period were in the range from 81 to
83° C. When the monomer addition was finished 0.15 parts by
weight ammonium peroxydisulfate in 5 parts by weight water were
added, heating was continued for 60 minutes and the reaction
mixture was cooled.

20 The pH was adjusted to 9.5 by means of 15 ml of 25 % NH₃;
the solids content was about 50 %.

E X A M P L E 2:

The example was performed as in Example 1, except aceto-
acetic acid allyl ester was omitted in the polymerization.

25 E X A M P L E 3:

A monomer emulsion was prepared from
310 parts by weight water
9 parts by weight ammonium-tri-tertiary butyl phenol polyglycol
ether sulfate having about 6 ethylene oxide

units

12 parts by weight methacrylic acid

6 parts by weight acrylic acid

300 parts by weight 2-ethylhexyl acrylate

5 300 parts by weight methyl methacrylate and

16 18 parts by weight acetoacetic acid allyl ester,

64 276 by stirring in a rapid stirrer, until a stable emulsion was obtained.

16 1 In an apparatus as described in Example 1 a mixture consisting of

10 306 parts by weight water

3 parts by weight ammonium-tri-tertiary butyl phenol polygly-
col ether sulfate having about 8 ethylene
oxide units and

15 60 parts by weight monomer emulsion

was heated to 81° C and a solution of 0.45 parts by weight ammonium peroxydisulfate in 15 parts by weight water was added. The residual monomer emulsion was metered in and polymerization was carried to completion. The total time of addition was 2 hours,

20 the polymerization temperature and the temperature during the second heating period were in the range from 81 to 83° C. When the addition of monomers was terminated, 0.15 parts by weight ammonium peroxydisulfate in 5 parts by weight water was added, heating was continued for 1 hour and the reaction mixture was cooled. The pH was adjusted to 9.3 by means of 15 ml of 25 %

25 NH₃. The solids content was about 50 %.

E X A M P L E 4:

29 The example was carried out in an analogous manner as Example 3, except that acetoacetic acid allyl ester was omitted in the

polymerization.

E X A M P L E 5:

A monomer emulsion was prepared from
380 parts by weight water

5 6 parts by weight ammonium-tri-tertiary butyl phenol polyglycol
ether sulfate having about 8 ethylene oxide
units

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12 parts by weight methacrylic acid

6 parts by weight acrylic acid

10 12 parts by weight acrylamide

450 parts by weight ethyl acrylate

150 parts by weight vinyl toluene

18 parts by weight acetoacetic acid allyl ester

by stirring in a rapid stirrer, until a stable emulsion was obtained.

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In an apparatus as described in Example 1 a mixture consisting of

390 parts by weight water

20 3 parts by weight ammonium-tri-tertiary butyl phenol polyglycol
ether sulfate having about 8 ethylene oxide
units

3 parts by weight nonyl phenol polyglycol ether having about
30 ethylene oxide units and

60 parts by weight monomer emulsion

25 was heated to 81° C and a solution of 0.45 parts by weight
ammonium peroxydisulfate in 15 parts by weight water was added.
The residual monomer emulsion was then metered in and polymerization was carried to completion. The total time of addition was 2 hours, the polymerization temperature and the tem-

perature during the second heating period were in the range from 81 to 83° C. When the addition of monomers was terminated 0.15 parts by weight of ammonium peroxydisulfate in 5 parts by weight of water was added, heating was continued for 60 minutes and the reaction mixture was cooled. The pH was adjusted to 9.5 by means of 15 ml of NH₃ /25%). The solids content was about 45%.

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E X A M P L E 6:

The procedure was the same as in Example 5, except that acetoacetic acid allyl ester was omitted in the polymerization.

E X A M P L E 7:

In a 16 liter autoclave provided with an impeller stirrer there was introduced a liquor consisting of 3090 g of demineralized water 80.5 g of sodium dodecylbenzene sulfonate 15 g of potassium persulfate and 3 g of NaOH (solid).

The liquor and the whole apparatus were flushed with nitrogen. The other operations were also performed in a protective gas atmosphere.

From a recipient a mixture consisting of 1200 g of butadiene 1560 g of styrene

90 g of acetoacetic acid allyl ester was introduced by pumping into the autoclave.

The stirrer was set in motion (about 300 r.p.m.) and heating was started. The mixture was polymerized for 2 and a half hours at 70° C (the inner pressure was about 10 bars) and a solution consisting of

40 g of sodium dodecylbenzene sulfonate in
750 g of demineralized water was added by pumping.

After another 2 hours of polymerization at 70° C a solution
of

5 15 g of potassium persulfate in
250 g of demineralized water was added and a mixture consisting of
180 g of styrene and
60 g of acrylic acid was metered in the course of about 15 minu-
tes.

10 The after-reaction time was 3 hours (also at 70°). There-
after the vessel was cooled, ventilated and the product was fil-
tered.

15 The solids content was about 42 %. The quantity of coagulate
was low.

15 E X A M P L E 8:

The procedure was the same as in Example 7, except that the
quantity of styrene (1740 g) was replaced by vinyl toluene.

20 E X A M P L E 9:

The procedure was the same as in Example 7, except that
half of the quantity of styrene (780 g in the recipient and 90 g
in the second addition) was replaced by vinyl toluene.

25 COMPARATIVE EXAMPLE 10: (not in accordance with the present
invention)

As described in Example 7 a dispersion was prepared, but
the acetoacetic acid allyl was omitted and the amount of water
was reduced by 90 g to 3000 g.

29 To prepare the dispersion paints according to the invention
having a high wet adhesion the dispersions obtained according
to the preceding examples were blended with a pigment suspension.

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Pigment suspensions or pigment pastes of this type, which are suitable for making dispersion paints of low pigment content and especially gloss paints consist, for example, of titanium dioxide uniformly dispersed in water. They contain, in general, protective colloids such as cellulose derivatives, for example hydroxyethyl cellulose, and dispersing agents, for example salts for poly(meth)acrylic acid or sodium polyphosphate. Usual constituents of pigment suspensions are furthermore antimicrobial preserving agents, anti-foaming agents, pH stabilizers and filters. Especially suitable titanium dioxide pigments are the rutile and anatase modifications. For the manufacture of gloss paints the average particle diameter of the pigment should be near the lower limit of the light wave length, i.e. at about 0.4 to 0.2 micron. For making dull paints of low pigment content special large surface silicate pigments could be concomittantly used. Dull paints of high binder content yield paint coatings that are easily to clean. The pigment paste may, of course, also contain colored pigments or the desired shade is obtained by adding a shading dyestuff to the dispersion paint containing the white pigment.

The pigment suspension can be prepared in known manner, for example by dispersing the pigment in a dissolver, a ball mill or sand mill. For use in gloss paints the pigment suspension should not contain noticeable amounts of pigment aggregates which would affect the gloss.

Auxiliaries such as plasticizers, cross linking agents, buffer substances, thickening agents, thixotropic agents, rust preventing agents, alkyd resins, or drying oils may be added to the dispersion or the dispersion paint. Suitable plasticizers

are not the solvents initially mentioned as film consolidation agents with temporary action but compounds which reduce the film forming temperature and remain in the polymer for a longer period of time, for example dibutyl phthalate.

To test the wet adhesion dispersion paints were prepared as follows:

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Recipe I:

1. 41.0 parts by weight water *(Registered Trade Mark)*
15.6 parts by weight of a 3 % aqueous solution of Tylose *(Registered Trade Mark)*

H 20

(Registered Trade Mark)

0.4 part by weight Calgon *(N)* (solid)

3.0 parts by weight dispersing agent PA 30

1.0 part by weight ammonia of 25 % strength

2.0 parts by weight of preserving agent

3.0 parts by weight of anti-foaming agent

175 parts of titanium dioxide having a particle size of
from 0.2 to 0.4 micron

10 parts 1,2-propylene glycol were dispersed and

2. 710.0 parts by weight of dispersion of Examples 1 - 6 having a solids content of about 50 % and 843 parts by weight of dispersion of Examples 7 to 10 having a solids content of 42 % was used, whereto 2.0 parts by weight of ammonia of 25 % were added, if the pH was not superior to about 7.

3. A mixture of

10 parts by weight butyl diglycol acetate,

27.0 parts by weight 1,2-propylene glycol

was slowly added while stirring.

The liquid or soluble components indicated sub 1 except 1,2-propylene glycol were introduced into a vessel provided with a stirrer in the aforesaid order and the pigment was dis-

solved therein by means of a dissolver. 1,2-Propylene glycol was added thereafter. This pigment paste was prepared in a large amount so that for the blends with the dispersions to be tested equal conditions, for example as regards the pigment dispersion, were ensured.

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Recipe II differed from recipe I by a different composition of the mixture of solvent added to the finished paint (processing step 3 of the preparation of paint). A mixture of 36 parts by weight of 1,2-propylene glycol, 13.5 parts by weight of butyl diglycol acetate and 20 parts by weight 2,2,4-trimethylpentanediol-1,3-monoisobutyrate-1 (trade name: Texanol) was added.

10 Recipe III:

15 Recipe III also differed from the aforesaid recipes by a different composition of the mixture of solvent added to the finished paint, i.e. a mixture of 51.1 parts by weight of 1,2-propylene glycol, 18.9 parts by weight of butyl diglycol acetate and 20 parts by weight of 2,2,4-trimethylpentanediol-1,3-monoisobutyrate *sold under Registered Trade Mark* (trade name: Texanol) was added.

20 For the manufacture of the individual paints a corresponding proportion of the pigment paste was mixed, while slowly stirring, with the dispersions approximately one day old, whereupon the solvents mentioned sub 3) were added. After complete confection, the paints were passed through a sieve.

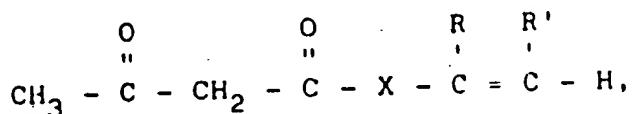
25 The paints were allowed to stand for one day and then spread on glass plates and steel sheets onto which a pigment-ed glossy air-drying alkyd resin enamel had been sprayed and which had been kept after drying for 24 hours at 100° C. A film applicator was used having a slit diameter of 200 microns.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

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1. A process for the preparation of aqueous plastics dispersions suitable for making paints having a high wet adhesion, by copolymerization in an aqueous medium under conventional conditions of the following monomers:

- A) from 20 to 79.4% by weight, preferably 40 to 60% by weight, calculated on the total quantity of the monomers, of the hardening monomers methyl methacrylate, styrene and vinyl toluene or a mixture thereof,
- B) from 20 to 79.4% by weight, preferably 40 to 60% by weight, calculated on the total quantity of the monomers, of monomers, having a plasticizing effect in the polymer, selected from the group of acrylic acid esters carrying in the alcohol radical a linear or branched alkyl radical having from 2 to 8 carbon atoms or conjugated dienes having from 4 to 8 carbon atoms optionally substituted by halogen,
- C) from 0.1 to 5% by weight of acrylic acid, methacrylic acid, acrylamide, methacrylamide or mixtures of these, which comprises using additionally in the polymerization
- D) from 0.5 to 10% by weight of an acetoacetic acid ester of the formula



wherein R is H or CH_3 , R' is H or CH_3 , and X is $-\text{O}-$, $-\text{O}-\text{CH}_2$ or $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}-$.

2. Process as claimed in Claim 1, which comprises using simultaneously in the polymerization from 1 to 5% by weight of

acetoacetic acid ester.

3. Process as claimed in Claims 1 or 2, which comprises using simultaneously as acetoacetic acid ester acetoacetic acid allyl ester.

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